A COMPUTATIONAL THERMODYNAMIC MODEL OF AL-AU-GE-SI QUATERNARY SYSTEM

A Thesis
Presented in Partial Fulfillment of the Requirements for
the Degree Graduation with Distinction in the
Graduate School of The Ohio State University

By
Yifan Jiang.

The Ohio State University
2011

Honor's Thesis Examination Committee:
Approved by
Dr. Ji-Cheng Zhao, Adviser
Dr. Charles Drummond

ABSTRACT

Compositionally abrupt junctions (interfaces) in Ge-Si heterostructure nanowires can optimize the performance. However, traditional vapor-liquid-solid (VLS) method using Au droplet may cause “reservoir effect”, leading to interface diffuseness. In this case, vapor-solid-solid (VSS) method can be applied along with VLS method. AlAu alloy are used as a catalyst to raise the eutectic temperature. In order to determine which AlAu alloy and temperature are the best for nanowire generation, the Al-Au-Ge-Si quaternary database was established using thermocalc software. Using gibbs free energy expressions for binary systems, the phase diagrams of ternary systems were calculated and compared with experimental data. Calculated Al-Ge-Si and Au-Ge-Si phase diagrams show similar eutectic structures and are in good agreement with experimental data. However, considerable solubility was found in Al_2Au compound, raising the eutectic temperature and changing the liquidus lines of the compound. After comparing different AlAu compounds, the alloy that is best for Ge-Si formation are $AlAu_2$ and AlAu alloys because they shows both low solubility of semiconductor and relatively high eutectic temperatures.

VITA

March 18, 1989 …….....Born, Suzhou, Jiangsu, China.

2007 ……...High School Graduation, Shanghai, China

PUBLICATIONS

None.

FIELDS OF STUDY

Major Field: Materials Science and Engineering

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1

INTRODUCTION AND LITERATURE REVIEWS

The purpose of this project is to develop and assess a thermodynamic model for Al-Au-Ge-Si quaternary system so that it can be used to predict the proper temperature and catalyst to produce Ge-Si nanowires.

Thermodynamics and phase diagrams are important in the development of new alloys and the processing of materials. The prediction of material behavior has started to be the main focus of material processing due to the cost and time consuming experiments. Thermodynamic calculations based on CALPHAD (Calculations of Phase Diagrams) [1] have become popular in the industry as many materials involve complex chemical reactions and phase equililbria during synthesis or processing. Knowing the thermodynamic data of simple phases and pure elements, it is possible to predict the more complex phases before doing any experiments.

1.1 Ge-Si Nanowires Formation

The project of calculating the phase diagram of the Al-Au-Ge-Si quaternary system comes from the idea of producing adrupt interfaces in a heterogeneous Si-Ge nanowire. Nanowires have got an increasing attention these years. The fact that electrons in nanowires are quantum confined laterally leads to a special feature of nanowires that the

electrons occupy energy levels different from the bulk materials [2]. The discrete values of electrical conductance make nanowires important to electronic related devices. As a relatively "young" material, a nanowire will continue to develop until it can be applied to industrial use.

A Si-SiGe nanowire is a semiconducting nanowire with axial heterostructure and can be used in tunnel field-effect transistors and thermoelectric devices. The optimal performance of nanowire comes from the formation of compositionally adrupt and structurally perfect junctions (interfaces) [3]. It was usually synthesized by the vapor-liquid-solid (VLS) method with the catalyst of metals such as Au [4]. VLS method is performed using eutectic reaction between semiconductor and metal. By having liquid metal reacting with vapor-phase semiconductor such as SiH_4 or GeH_4 above the eutectic temperature, semiconductor atoms dissolve into the liquid metal. Once the concentration of semiconductor (Ge or Si) reaches supersaturation in the droplet, the semiconductor precipitates at the the liquid-solid interface and grows as a nanowire.

Although a heterostructure Si-GeSi nanowires can been grown successfully using VLS method, the interface diffuses due to the "reservoir effect" –since the solubility of Ge and Si are high in Au liquid, it is slow to deplete one semiconductor in the droplet before a different semiconductor can be deposited [3]. In this case, a vapor-solid-solid (VSS) was developed to reduce the solubility of semiconductor. Si nanowires are first grown using VLS method before the temperature reduces below the eutectic temperature (T_{eu}) for VSS method. Al are added to Au as a catalyst in order to raise the eutectic temperature with Si and Ge so that nanowires can grow at reasonable rate during VSS mechanism. Wen et al.'s research suggested using $AlAu_2$ as catalyst [3]. The phase diagrams generated in this

research aims to make sure which AlAu alloy would provide the best condition to grow Ge-Si nanowires.

1.2 Previous Thermodynamic Researches

The thermodynamic data and phase diagrams of the Al-Au-Ge-Si system are important for the understanding of the roles of Au and Al catalysts in the formation of Si-Ge nanowires. The Si-Ge nanowire with the catalyst of Au was studied by Sa et al. in 2008[4]. The study focused on the size dependence of the $Si_{1-x}Ge_x$ alloy composition with the vapor-liquid-solid method originated from the capillarity effect.

The Al-Au-Ge-Si quaternary system consists of six binary systems, Al-Au, Al-Ge, Al-Si, Au-Ge, Au-Si, and Ge-Si. The phase diagrams of these binary systems have already been established. The quaternary system also consists of four ternary systems, Al-Au-Ge, Al-Au-Si, Al-Ge-Si, and Au-Ge-Si, which have not been optimized yet.

According to the previous researches, the Al-Au system is a complex binary system important for understanding the metallization behavior of semiconductor devices. In 2004 Li et al. evaluated all the previous experimental and thermodynamic data and optimized this binary system with ten different phases [5], of which Al_2Au is the most stable phase. The optimized Al-Ge eutectic system was shown to consist of three phases: the liquid, the Al fcc solid solution and Ge diamond cubic solid solution [6]. The Al-Si eutectic system generated in 2000 [7] has a similar phase structure with the Al-Ge system due to the similar structure between Si and Ge. The Au-Si binary system is also a simple eutectic system, with the optimized thermodynamic parameters shown in the research by Meng et al. in 2007 [7], and the most recent study on Au-Ge binary systems was conducted in

2009 [9] . The phase diagram of Al-Au [5] is shown below in Figure 1 and .the phase diagram of Au-Si [7] is shown in Figure 2. Since Al-Au is a complexed system, it is necessary to determine which phase to use as a catalyst for the synthesis of Ge-Si nanowire.

With the binary systems fully optimized, the ternary systems have not been studied a lot. There are limited experimental and calculation data for Al-Ge-Si, Au-Ge-Si, and Al-Au-Si systems. For Al-Au-Si system, after the 70 at.% Au, Al_2Au-ternary, Al-$Al_{0.5}Au_{0.25}Si_{0.25}$ vertical sections and the liquidus projection at 1100℃ were obtained in 1995 [10], Hoch further calculated the Au_2Al-Si and Al_2Au-Si vertical sections in the same year [10].

For the last ternary system –Al-Au-Ge, no experimental data are available.

2

THERMODYNAMIC MODELS

An alloy system usually contains solid solutions and intermediate compounds. The thermodynamic model was established according to the three thermodynamic laws that the system is at equilibrium when the Gibbs free energy is at a minimum. The Gibbs energy for pure elements, the free energy for regular solution and the excess free energy can be expressed as functions of temperature and conpositions. The equations below show how to calculate the parameters for these phases. The existing expressions are all empirical based and have been assessed over years.

Eq. (1) shows the equation used for calculation of the free energy of a pure element, in which ${}^{0}G_i^{\varphi}$ represents the standard free energy for element *i* at phase φ, *T* represents the temperature and constants *a, b, c, d, e, f, g, and h* are parameters.

$$ {}^{0}G_i^{\varphi}(T) = a + bT + cT\ln(T) + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \quad (1) $$

The solution model was made assuming substitutional solution. The equation for regular solution (liquid, solid solution) is shown in Eq. (2)

$$ G_m^{\phi} = \sum_{i=elements}^{n} x_i^0 G_i^{\phi} + RT \sum_{i=elements}^{n} x_i \ln(x_i) + G^{ex,\phi} \quad (2) $$

in which x_i is the mole fraction of element i in phase ϕ. G_i^{ϕ} is expressed in Eq.(1). $G^{ex,\phi}$ represents the excess free energy, usually shown by Redlich-Kister polynomial,

$$G^{ex,\phi} = \sum_{\substack{i,j=1 \\ (i \neq j)}}^{n} x_i x_j \sum_{p=0,1,\ldots}^{m} {}^{p}L_{(i,j)}^{\phi}(x_i - x_j)^p \tag{3}$$

The term in Eq. (3) illustrates the binary interaction for i–j binary system, where ${}^{p}L^{\phi}_{(i,j)}$ is the binary interaction parameter, and can be represented by ${}^{p}L^{\phi} = a_p + b_pT$, where a_p and b_p are constants and can be determined from experimental data (e.g., phase diagram) using least-squares method. This determination of coefficients from experimental data is known as thermodynamic optimization.

The Gibbs energy of a binary stoichiometric phase is given by Eq. (4)

$$G^{\varphi}_{stoichiometric} = \sum_{i=1}^{n} x_i^0 G_i^0 + \Delta G_{\mathrm{f}} \tag{4}$$

where $G_f = c + dT$ represents the Gibbs energy of formation per mole of a stoichiometric compound, in which c and d are constants, obtained from experimental data.

3

CALCULATION PROCEDURES

The databases from the six binary systems were established from the existing paper. The expressions for Gibbs free energy were written in the functions shown in the introduction section. The expressions for single elements in various states including liquid, diamond and face center cubic (fcc) phases were extracted from the Thermocalc software. The binary interaction parameters ${}^{p}L^{\varphi}_{(i,j)} = a_p + b_p T$ (p=0,1,…) and free energy of stoichiometric compound formation ($\Delta G_f = c + dT$) were extracted from the previous paper talking about binary phases. Binary phase diagrams were then generated using the databases.

The ternary system databases were built using related binary system data. The functions for the same phase were put together. The ternary interaction parameters ${}^{p}L_{(i,j,k)}$ for solution phases are assumed to be zero during the evaluation of database. The isotherms, isopleths and liquidus projection of ternary systems were plotted and compared with the experimental data found from the ASM website.

4

RESULTS AND DISCUSSION

4.1 Binary Systems

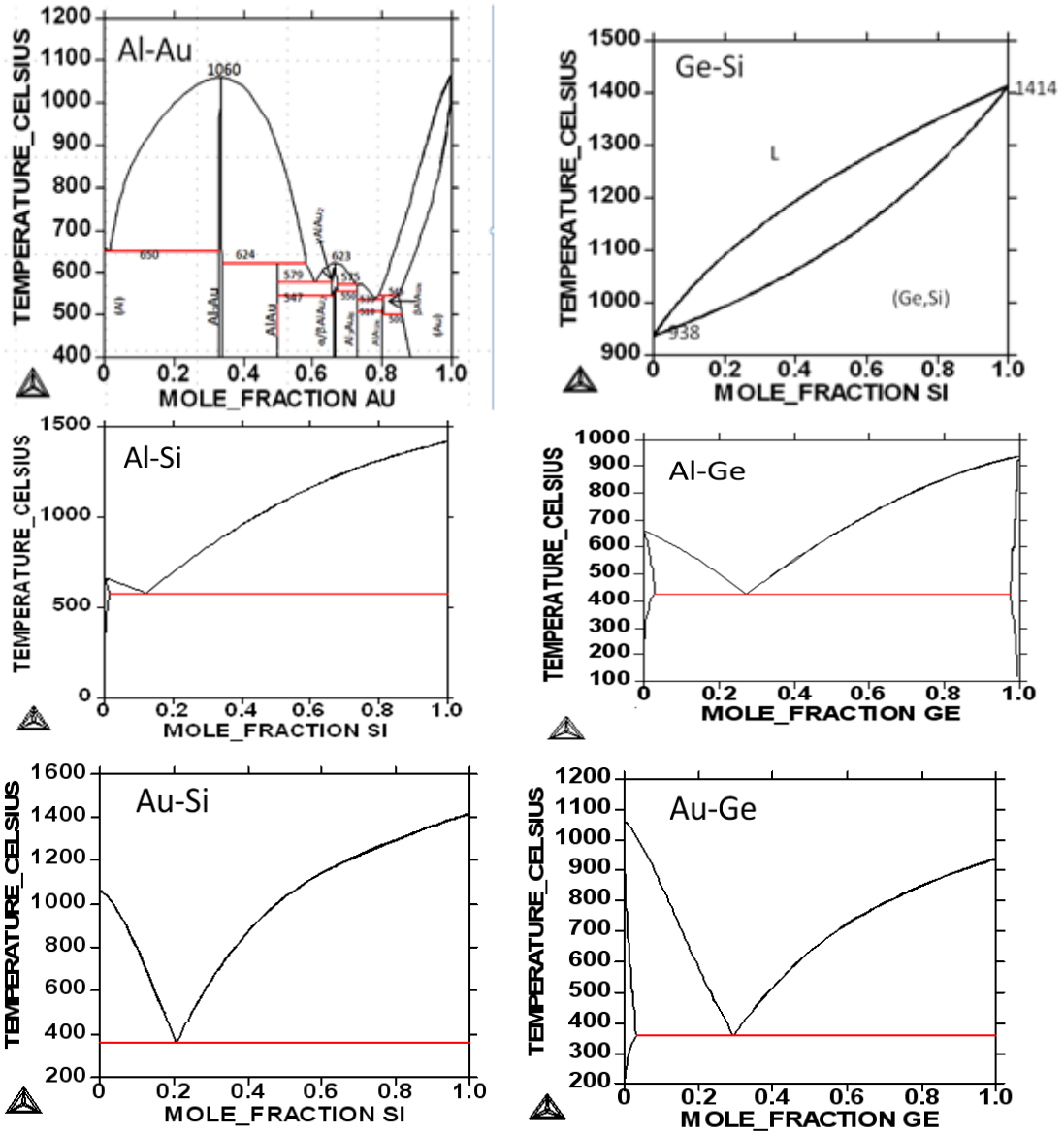

Figure 4.1: Binary Phase Diagrams

The six binary phase diagrams were plotted and shown in **Figure 4.1**.

As is expected, the Al-Au system shows complicated structure with several different stoichiometric compounds. Ge-Si system is a simple binary system and assumed as an ideal solution, so the binary interaction parameter for this system was set to be zero. The rest four binary systems are simple eutectic systems, all showing liquid, fcc (Al/Au), and diamond (Ge/Si) phases. The eutectic temperatures and compositions were calculated and shown in **Table 4.1**.

Table 4.1: Euctectic Composition and Temperature for Binary systems

Binary Systems	Eutectic Temperature (°C)	Eutectic Composition (at% Si/Ge)
Al-Ge	424.89	27.33
Al-Si	575	12.18
Au-Ge	358	29.4
Au-Si	364	20.7

It is indicated from the table that Si shows a lower solubility in Al and Au than Ge does, whereas Ge can dissolve more metals than Si does.

4.2 Ternary Systems

The ternay systems were plotted and compared with the existing experimental data.

4.2.1 Al-Ge-Si and Au-Ge-Si

Since all the related binary systems for the two ternary systems are eutectic systems, the two ternary systems are simple eutectic systems, with liquid, fcc(Al/Au), diamond, and diamond(Ge, Si) phases.

4.2.1.1 Isothermal Diagrams

The isotherms of the two ternary systems were plotted between temperature range 500K and 1400K.

Isothermal diagrams show the horizontal sections of the ternary system. According to the phases shown from the isothermal diagrams, the melting temperature and the liquidus temperature of the systems could be estimated. Shown in **Figure 4.2**, the Al-Ge-Si isothermal diagram is calculated at 800K. In the diagram, green lines are tie-lines that indicate two-phase region and connect the related single phases. The red outlined region is the three-phase region and the black outlined region is the single-phase region. Since the three-phase region is only observed as a line, the intersection point between three-phase region and liquid region shows the eutectic temperature.

Table 4.2: Eutectic Temperatures in Al-Ge-Si and Au-Ge-Si

	Al-Ge-Si	Au-Ge-Si
T_{eu} (K)	~800	~630
T_{eu} (℃)	~577	~357

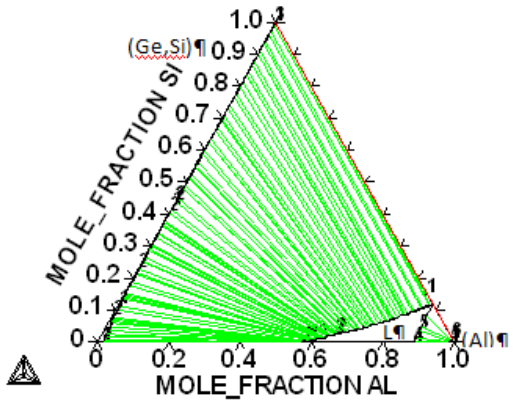

Figure 4.2: Al-Ge-Si Isotherm at 800K

The isothermal diagram for Au-Ge-Si is also calculated to find the eutectic temperature. The eutectic temperatures of the two ternary systems are shown in **Table 4.2**..It is discovered that the eutectic temperature of ternary systems increases a lot from that of binary systems. The eutectic temperature for the AlAu alloy to be estimated would be between the range of 357℃ and 577℃.

4.2.1.2 Liquidus Projection

The liquidus projections also show the change of liquidus line of the two ternary systems. The two calculated data were compared with the experimental data. The black lines on the projection show the isothermal liquidus lines, whereas the final red line indicates the eutectic temperature and composition. The comparisons between experimental and calculated diagrams are shown in **Figure 4.3** and **Figure 4.4**.

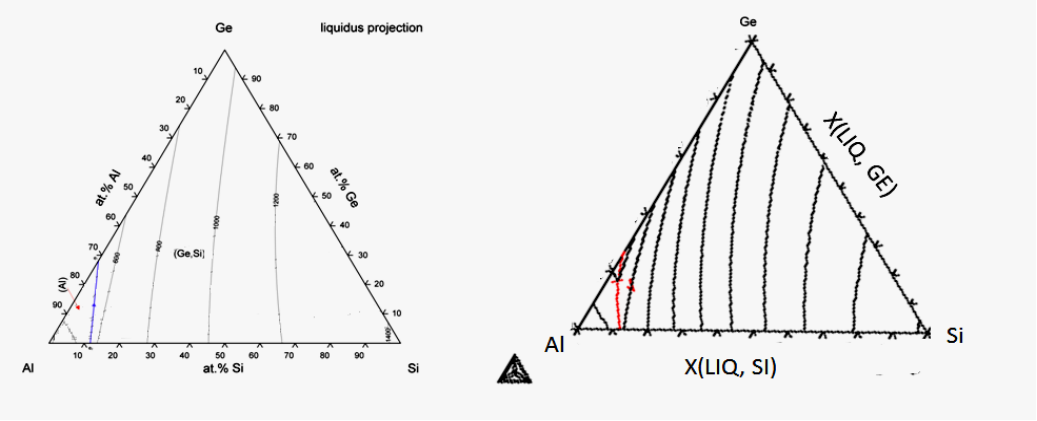

Figure 4.3: Comparison Between Experimental [12] and Calculated Liquidus Projection for Al-Ge-Si from 400℃ to 1400℃.

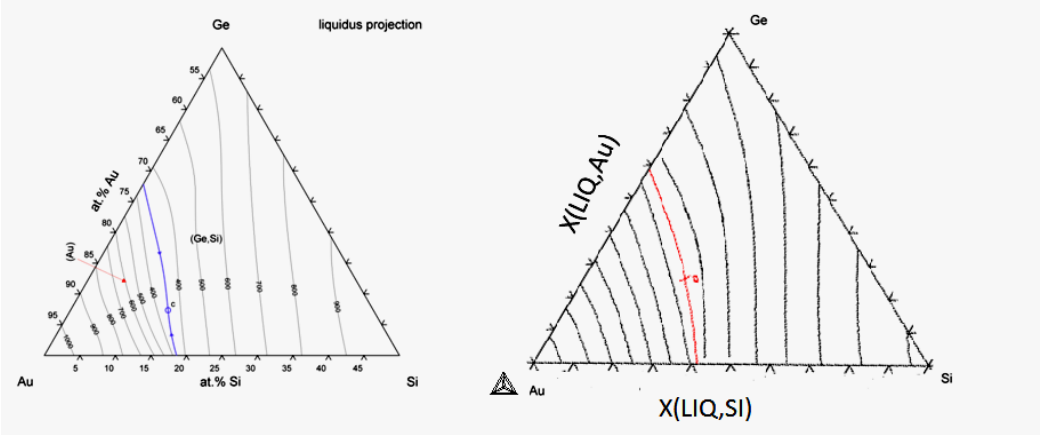

Figure 4.4: Comparison Between Experimental [13] and Calculated Partial Liquidus Projection (0-50%Si, 50%-100%Au) for Au-Ge-Si from 350℃ to 1000℃.

It is shown from the figure that the calculated values are in reasonable agreement to the experimental data so the eutectic temperature obtained from calculation can be used for further exploration and don't need much assessment.

4.2.1.3 Isopleth Digrams

The isopleths of the two ternary systems were also calculated and compared with the existing experimental data. Isopleths show vertical sections of the phase diagram and can review exactly how the phases change with temperature at a certain composition. The sample comparison diagrams for Al-Ge-Si system are shown in **Figure 4.5**.

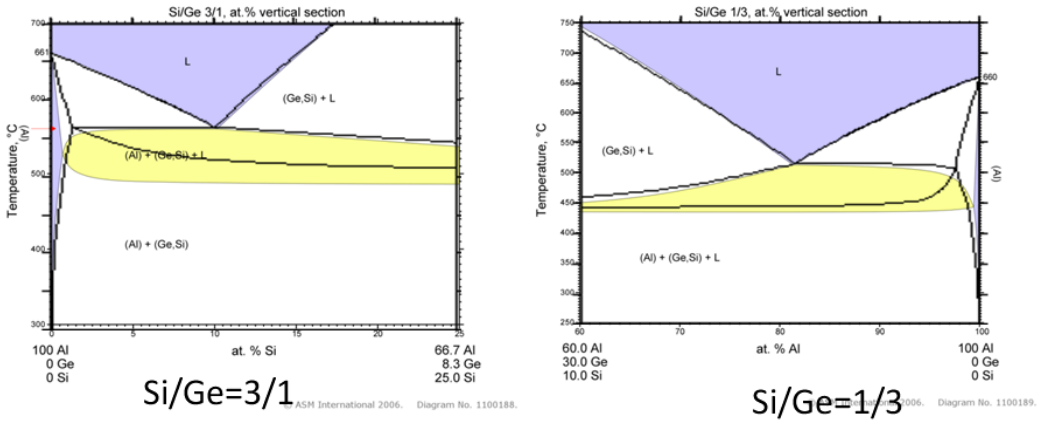

Figure 4.5: Al-Ge-Si Isopleth Comparison at Si/Ge =3/1 and Si/Ge=1/3 [14]. The yellow region is the three phase region from experimental data. The dark blak lines are calculated diagrams.

It is shown that the when Si/Ge ratio is small, the experimental data has a better agreement with the calculated values. This is reasonable because Si has a lower solubility in metal than Ge.

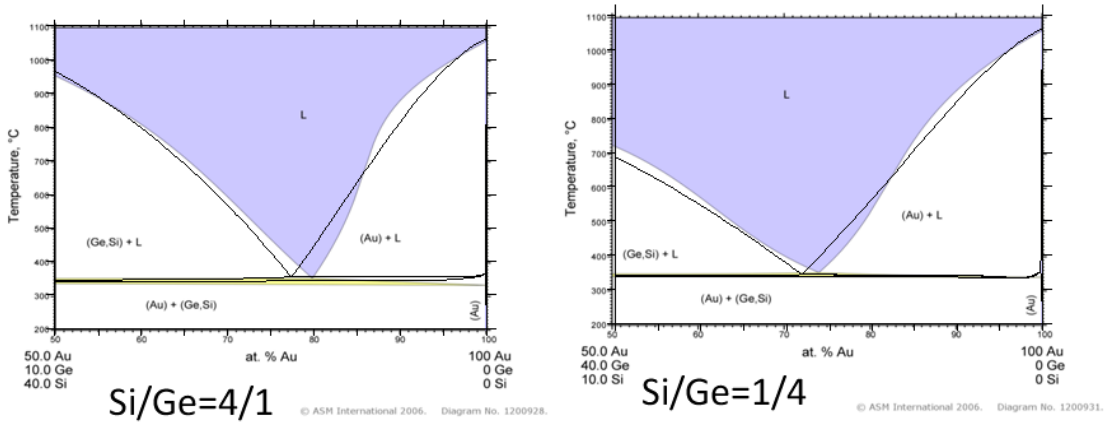

Figure 4.6: Au-Ge-Si Isopleth Comparison at Si/Ge =4/1 and Si/Ge=1/4 [13]. The yellow region is the three phase region from experimental data. The dark blak lines are calculated diagrams.

The comparison diagram for Au-Ge-Si system is shown in **Figure 4.6**. The calculated eutectic temperature and melting temperature all agreed well with experimental data. However, both calculated eutectic compositions are around 2 at% Au smaller than the experimental ones. It will be taken into account for further assessment.

4.2.2 Al-Au-Si System

The Al-Au Si system was the one that was expected to have large difference between calculation and experimental data because there are a lot of stoichiometric phases involved that the energy of mixture remains unknown.

The isopleths diagrams were plotted and compared with the experimental data. The isopleths at Al/Si=1/1 shown in **Figure 4.7**. As is shown from the diagram, the calculated eutectic temperature for the ternary system agreed with the experimental data, however, there is a large difference around the liquidus lines of Al_2Au. An possible reason might be that there is considerable solubility of Si in the Al_2Au compound, changing the liquidus temperature of Al_2Au.

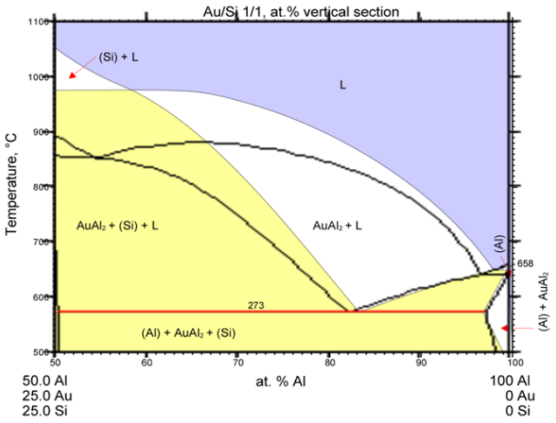

Figure 4.7: Al-Au-Si isopleths at Au/Si=1/1 comparison [10]. The yellow region is the three phase region from experimental data. The dark blak lines are calculated diagrams. The red line is the calculated eutectic temperature.

In order to determine the appropriate AlAu alloy for Ge-Si nanowire production, the isopleths of different compounds were plotted and shown in **Figure 4.8**.

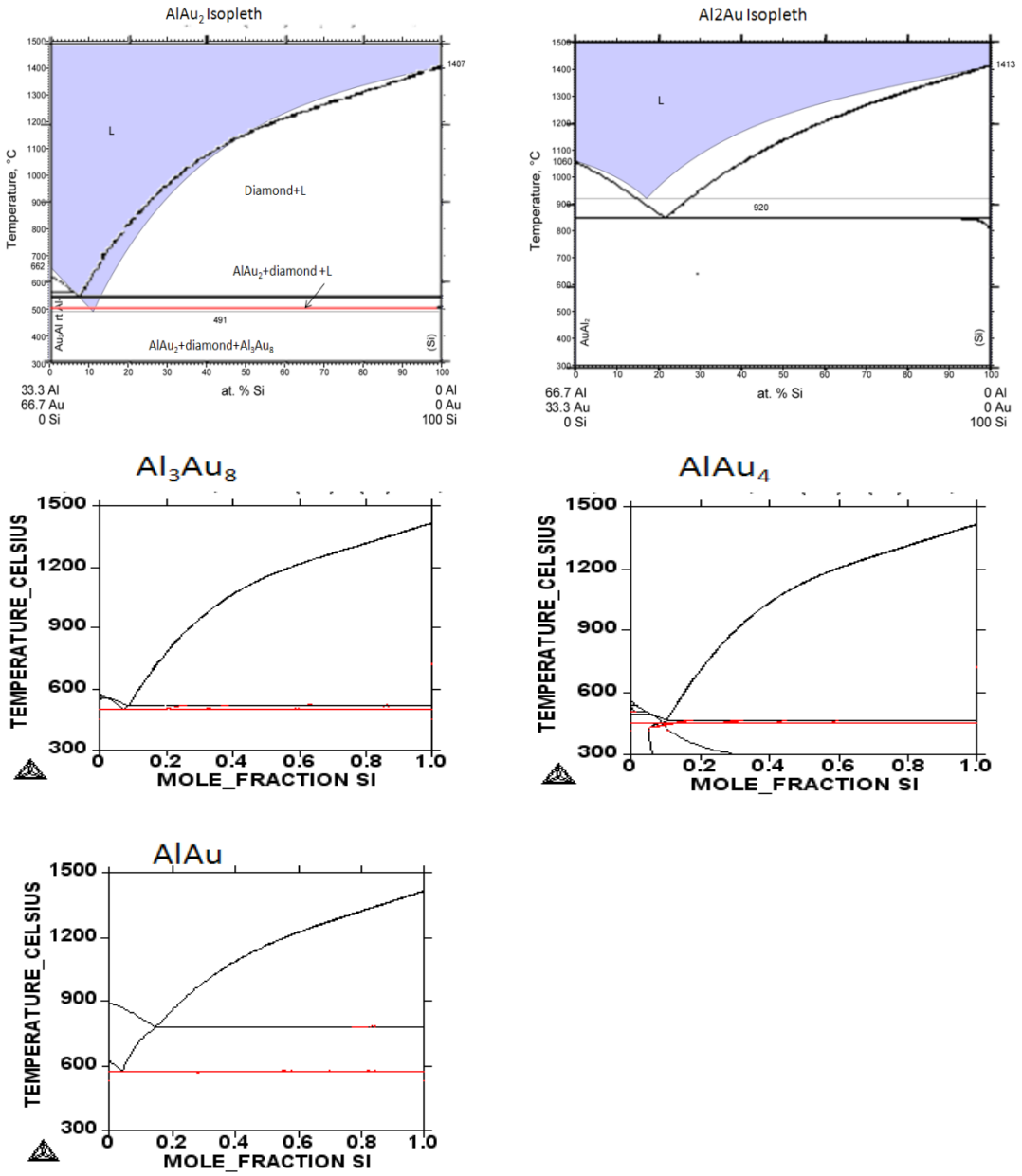

Figure 4.8: Eutectic Isopleths for AlAu alloys in Al-Au-Si system

The experimental data for $AlAu_2$ and Al_2Au isopleths is obtained [11] and compared. The ternary eutectic composition for Si and temperature is shown in **Table 4.3**.

4.2.3 Al-Au-Ge System

Due to lack of experimental data in Al-Au-Ge system, this ternary system was compared with the Al-Au-Si system since Ge and Si show similar structure. The isopleths are also plotted for different AlAu alloys in **Figure 4.9** and the eutectic information is shown in **Table 4.3**

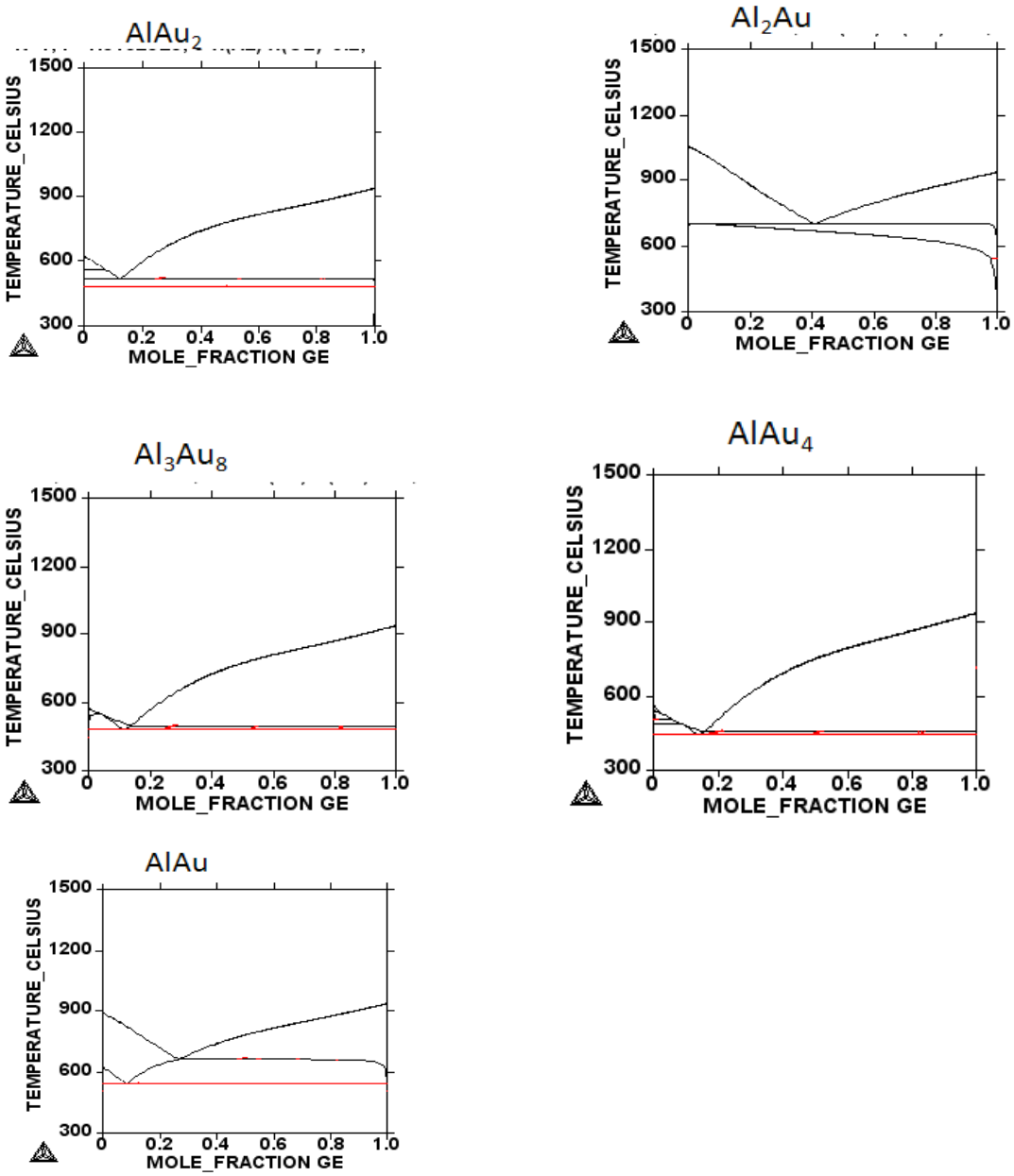

Figure 4.9: Eutectic Isopleths for AlAu alloys in Al-Au-Ge system

4.2.4 Eutectic Comparison and Proper AlAu Alloy Selection

Comparing the eutectic temperature and composition for different stoichiometric compounds in Si and Ge, it is found that the eutectic eutectic temperatures for the same stoihiometric compound in the two ternary systems do not vary a lot.

Table 4.3: Calculated Eutectic Temperature for Al-Au-Si and Al-Au-Ge system

Stoichiometric Compound	Eutectic Composition (at% Si)	Eutectic Temperature (℃) (Al-Au-Si)	Eutectic Composition (at% Ge)	Eutectic Temperature (℃) (Al-Au-Ge)
Al_2Au	22.62	850	41.33	683.6
$AlAu_2$	8.3	550	12.87	506.2
Al_3Au_8	7.7	490.2	11.58	472.1
$AlAu_4$	10.62	447.9	15.90	447.9
AlAu	4.9	562.7	9.67	532.5

In order to find the best catalyst for nanowire generation, the eutectic temperature should be between that of Au-Ge-Si eutectic temperature (~357℃) and that of Al-Ge-Si eutectic temperature (~577℃) so that the VSS mechanism would perform in reasonable reaction rate. Within the acceptable range, higher eutectic temperature preferred to get maximum efficiency. Lower eutectic composition of Ge and Si is also desired for the composition in order to avoid the "reservoir effect" at the nanowire interface.

It is found that although Al_2Au is the most stable stoichiometric compound in the Al-Au binary system, due to its high eutectic temperature and high ability to dissolve the semiconductors, it is not suitable as a catalyst alloy.

Among the rest four stoichiometric compounds, $AlAu_2$ and AlAu have relatively high eutectic temperature and low solubility of Si and Ge, which are suitable for the Ge-Si

nanowire growth. The suitable temperatures are between 550℃ and 600℃ during the VLS process, and slightly below 500℃ during VSS process.

5

CONCLUSIONS

A thermodynamic model was developed for Al-Au-Ge-Si using gibbs free energy of binary systems in thermocalc software. The model is used to evaluate the most proper temperature and composition for Ge-Si nanowire generation using Al-Au alloy as a catalyst.

The formation of compositionally abrupt axial heterojunctions in Ge-Si nanowires could give an optimal performance when it is used in the thermoelectric devices and transistors. Au is usually used in VLS method to create the abrupt interface, but the interface show diffuseness due to the high solubility of Ge and Si in liquid Au (more than 20% solubility), resulting in a long time to deplete the dissolved semiconductor before another one could react. In order to lower the solubility of Ge and Si, VSS method is used after VLS as a solid catalyst is applied below the eutectic temperature. Higher eutectic temperature is preferred for VSS process to improve nanowire growth. Al is considered to create proper AlAu alloy in the study.

Six binary thermodynamic systems that had already been modeled and assessed were collected and calculated. The binary phase diagrams show that Ge has larger solubility than Si, so it is considered that the *x* content of Ge_xSi_{1-x} nanowire should be kept low to avoid reservoir effect.

The ternary systems were then calculated assuming that the missing free energy parameters in solution phases and stoichiometric phase were zero. The calculated Al-Ge-Si and Au-Ge-Si ternary eutectic systems show reasonable agreement with experimental data. The eutectic temperatures for the two systems were calculated. The Al-Au-Ge and Al-Au-Si systems show reasonable similarity due to the similar structure between Si and Ge. In Al-Au-Si system, different isopleths show that there should be some solubility of Si in different alloys so that the calculated liquidus lines and eutectic temperatures were in large difference from the experimental data. The eutectic temperatures and compositions of each AlAu alloy were calculated for Al-Au-Ge and Al-Au-Si systems. Similar eutectic temperatures were observed for the same alloy in different systems. According to the criterions to select the proper AlAu alloy, $AlAu_2$ and AlAu were considered reasonable candidates since they have high eutectic temperature and allow low semiconductor solubility.

The next step of the study would be obtaining experimental data such as differential scanning calorimetry (DSC) experiments to get more specific data about liquidus lines of Al-Au-Ge and Al-Au-Si systems. The ternary systems would be able to be assessed at that time to generate more accurate temperature and composition range for the nanowire production.

BIBLIOGRAPHY

1. N. Saunders, A.P. Miodownik. CALPHAD (Calculation of Phase Diagrams). Pergamon, 1998.

2. Bhushan, Bharat (2004). Springer Handbook of Nanotechnology. (pp: 99). Springer - Verlag.

3. Wen, C -Y. "Formation of Compositionally Abrupt Axial Heterojunctions in Silicon-Germanium Nanowires." Science, Vol. 326 Issue 5957, (2009), 1247-1250.

4. I. Sa, B.-M. Lee, C.-J. Kim, M.-H. Jo, B.-J. Lee. "Thermodynamic analysis for the size-dependence of $Si_{1-x}Ge_x$ nanowire." CALPHAD, Vol.32 (2008).669-674

5. M. Li et al. "Thermodynamic assessment of the Al–Au system." Journal of Alloys and Compounds Vol.385 (2004): 199-206.

6. F. Islam, A.K. Thykadavil, M. Medraj. "Computational Thermodynamic Model of the Mg–Al–Ge System." Journal of Alloys and Compounds Vol.425 (2006): 129-139.

7. Y. Liu, G. Shao, P. Tsakiropoulos. "Thermodynamic reassessment of the Mo-Si and Al-Mo-Si systems." Intermetallics Vol.8 (2000): 953-962.

8. F.G. Meng, H.S. Liu, L.B. Liu, Z.P. Jin. "Thermodynamic Description of the Au–Si–Sn System." Journal of Alloys and Compounds Vol.431 (2007): 292-297.

9. J.Wang, C. Leinenbach, M. Roth, "Thermodynamic modeling of the Au–Ge–Sn ternary system." Journal of Alloys and Compounds Vol.481 (2009): 830–836.

10. F.H. Hayes and R. Schmid Fetzer "Aluminium-Gold-Silicon." Ternary Alloys Vol. 12 (1995): 106-114.

11. M, Hoch. "The Ternary system Aluminum-Gold-Silicon." Journal of Alloys and Compounds Vol.220 (1995): 27-31.

12. Song H., and Hellawell A., "Solidification in the System Al-Ge-Si: The Phase Diagram, Coring Patterns, Eutectic Growth, and Modification", Metall. Trans. A, Vol. 21, (1990), 733-740

13. Harmelin M., "Gold-Germanium-Silicon, Ternary Alloys", VCH, Vol. 13, (1995) 45-54

14. Hayes F.H., Longbottom R.D., Ahmad E., and Chen G., On the Al-Si, Al-Ge, and Al-Ge-Si Systems ana Their Application to Brazing in High Power Semiconductor Devices, J. Phase Equilib., Vol. 14, 1993, p 425-431.